

STATE OF CALIFORNIA
AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

STANDARD OPERATING PROCEDURES
FOR
AIR QUALITY MONITORING

APPENDIX M

PERFORMANCE AUDIT PROCEDURES
FOR
TOXIC AIR CONTAMINANTS LABORATORY AUDITS

MONITORING AND LABORATORY DIVISION

SEPTEMBER 2002

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M.1.0 INTRODUCTION

M.1.0.1 GENERAL INFORMATION

Performance audits of the Toxic Air Contaminants (TAC) laboratory program are performed semi-annually by the Quality Assurance (QA) Section staff. The purpose of the audits is to assess the accuracy of the methods used by the laboratories to measure ambient concentrations of TAC.

Audits are conducted by supplying each laboratory with two cylinders. One contains a mixture of standards, and one MTBE. Both are certified by the National Institute of Standards and Technology (NIST). The laboratory analyzes the contents of the cylinders following standard operating procedures and reports the results of the analysis to the QA Section. The QA Section in turn calculates the percent bias of the results and reports the final audit results to the laboratory. See Table M.1.0.1 for a list of toxic air contaminants that may be contained in the audit cylinders.

TOXIC AIR CONTAMINANTS

CHLOROFORM	CARBON TETRACHLORIDE
TRICHLOROETHYLENE	TETRACHLOROETHYLENE
BROMOMETHANE	DICHLOROMETHANE
1, 2-DICHLOROETHANE	1,1, 1-TRICHLOROETHANE
1,2-DIBROMOETHANE	VINYL CHLORIDE
1,3- BUTADIENE	BENZENE
TOLUENE	O-XYLENE
M-XYLENE	P-XYLENE
1,2 -DICHLOROPROPANE	CHLOROBENZENE
ETHYLBENZENE	TRICHLOROFLUOROMETHANE
TRICHLOROTRIFLUOROETHANE	DICHLORODIFLUOROMETHANE
ISOPRENE	STYRENE
1,2 -DICHLOROBENZENE	1,3 -DICHLOROBENZENE
MTBE (tert-Butyl methyl ether)	

Table M.1.0.1
Toxic Air Contaminants

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SEPTEMBER 2002

M.2.0 AUDIT PROCEDURES

M.2.0.1 AUDIT MATERIALS

1. Two toxics standards cylinders prepared by the National Institute of Standards and Technology (NIST).
2. Two 2-stage gas regulators (one dedicated for MTBE use only).

M.2.0.2 FIELD NOTIFICATION

Two weeks prior to the beginning of the quarter, contact the laboratories involved in the toxics audits to establish a preliminary audit schedule. Upon agreement of audit dates, mail an audit protocol along with a letter restating the audit period to each laboratory. See Figure M.2.0.1 for an example of a Schedule and Protocol Letter. The package should also include mailing forms to facilitate the return of the audit materials to the QA Section staff or transfer of the audit materials to another laboratory.

Below is a list of the laboratories involved in the toxics audits and their contacts:

Bay Area Air Quality Management District (BAAQMD)
Jim Hesson (415) 749-4625

Northern Laboratory Branch (NLB)
Hieu Le 323-4398 or send a note via e-mail at hle@arb.ca.gov

South Coast Air Quality Management District (SCAQMD)
Tai-Ching Hu (909) 396-2179

M.2.0.3 DELIVERY OF AUDIT MATERIALS

One week before the laboratory audit, arrange for delivery of the cylinders and gas regulators. Prior to shipping, check the regulators for leaks following the procedure described below. Once the regulators are determined to be free of leaks, they should be packed with extra cushioning to minimize the risk of damage during shipping.

Ensure audit materials leave the stock room one week prior to the audit. Contact the laboratory on the first day of the audit period to ensure that they have received the audit materials.

M.2.0.4 REGULATOR LEAK TEST

1. Securely install the regulator on a cylinder containing ultrapure air using the proper wrench and without forcing the connection.
2. Close the pressure adjusting knob (full counter-clockwise position) and the flow control valve. If the regulator is not equipped with a flow control valve, cap the gas delivery outlet.
3. Slowly, open the cylinder valve until the high pressure gauge indicates the full pressure of the cylinder.
4. Open the regulator pressure adjusting knob until the pressure on the delivery gauge reads 25 psi.
5. Close the cylinder valve and record the gauge readings.
6. Allow the system to sit for fifteen (15) minutes.
7. At the end of the testing period, check for pressure drop in both gauges.

NOTE: If there is a pressure drop in one or both gauges, get another regulator and perform a leak test. Send the malfunctioning regulator in for repairs.

8. Repeat procedure for both regulators.

M.2.0.5 SAMPLE ANALYSIS

The analytical laboratory takes an aliquot from the audit cylinder into a clean stainless steel canister. Following the Standard Operating Procedures (SOPs) for analysis of ambient air samples, the laboratory determines the concentration of the gases in the cylinder.

M.2.0.6 RETURN/TRANSFER OF AUDIT MATERIALS

1. At the completion of the audit period, the laboratory should immediately return the audit materials to the QA Section.
2. If the audit materials are to be sent from one laboratory to another, the laboratory which has just completed their audit period should immediately send the audit materials to the next laboratory. This will ensure that the audit schedule remains intact.



Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman

1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov



Gray Davis
Governor

April 17, 2002

Mr. Jim Hesson
Bay Area AQMD
939 Ellis Street
San Francisco, California 94109

Dear Mr. Hesson:

Thank you for participating in the upcoming toxics gases laboratory performance audit for 2002. Enclosed is a protocol that includes an audit cylinder schedule based on the requests of the participating laboratories. Per our discussions, your laboratory is scheduled to have the cylinders from May 6 to May 17, 2002. At the end of your scheduled time period, please have the cylinders and regulators sent to 1927 13th Street, Sacramento, California 95814, Attn: Mike Miguel. Please send the cylinders and regulators no later than May 17, 2002.

This performance audit should be representative of your normal sampling conditions. Briefly, you are to place an aliquot of the cylinder contents into a clean sampling container and analyze it using your normal procedures. In the interest of assuring and maintaining the operational integrity of the regulators, each will be leak tested by the Quality Assurance Section staff before being shipped.

I look forward to your participation in this performance audit. If you have any questions about the scheduling or the protocol, please call me at 324-6191.

Sincerely,

Michael Miguel, Manager
Quality Assurance Section
Monitoring and Laboratory Division

Enclosures

cc: Avi Okin, BAAQMD
Cliff Popejoy ✓
Tim Gergen

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.

California Environmental Protection Agency

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Figure M.2.0.1
Schedule and Protocol Letter

PROTOCOL

Biannual Performance Audit May 2002

Objective: The purpose of this performance audit is to confirm the comparability and assess the accuracy of the analytical methods currently used by participating laboratories measuring ambient concentrations of selected volatile organic compounds.

Audit Materials: Two gas regulators will be supplied by the Quality Assurance Section staff for use with the audit cylinders (also supplied). One cylinder will contain only MTBE (marked "MTBE") and one will contain a mixture of gases. Furthermore, one regulator will also be marked "MTBE". Please use the MTBE regulator only with the MTBE cylinder to avoid and contamination.

Participating Laboratories: The following laboratories will participate:

South Coast Air Quality Management District (SCAQMD) laboratory
Bay Area Air Quality Management District (BAAQMD) laboratory
California Air Resources Board:
Monitoring and Laboratory Division, Northern Laboratory Branch (NLB)

Schedule: The cylinders will be circulated to the participating laboratories. The order of distribution and the dates of the cylinder *arrivals* at the laboratories are as follows:

- | | | |
|----|--------|---------------|
| 1. | BAAQMD | May 6, 2002 |
| 2. | NLB | May 27, 2002 |
| 3. | SCAQMD | June 17, 2002 |

Delivery Arrangements: The audit cylinders and regulators will be hand delivered to NLB staff. For the other two labs, United Parcel Service standard air shipment will be used. Once you have completed your sample draw, please return the regulators and cylinders to:

California Air Resources Board
Monitoring and Laboratory Division
Michael Miguel, Manager
Quality Assurance Section
P.O. Box 2815
Sacramento, CA 95812

Please keep the cylinders and regulators no longer than two weeks after your arrival date above. Quality Assurance staff will coordinate via e-mail or telephone with each laboratory to ensure that the audit materials are delivered according to the performance audit schedule.

Figure M.2.0.1
Schedule and Protocol Letter (cont.)

Regulator Leak Check: The regulator should be attached to the audit cylinder, and the regulator valve closed. Open the cylinder valve and record the pressure reading displayed on the gauge. Adjust regulator flow control until the pressure on the flow gauge reads 25 pounds per square inch (PSI). Close the cylinder valve and let the system sit for 15-30 minutes. Note the readings on both gauges for any pressure drop. If a substantial drop (~50 PSI) occurs, notify Tim Gergen of the Quality Assurance Section at (916) 322-7053. Another regulator will be provided to you if the regulator is found faulty.

When shipping the regulators, please pack them in their original protective carton.

Sample Analysis: The participating laboratories are to use their standard operating procedures and existing standards in assaying gases from the performance audit cylinders. A portion of the cylinder gases should be placed in a clean sampling container for analysis. Do not analyze the gas directly from the cylinders. Each laboratory is asked to use no more than 200 liters of compressed gas from the cylinders (approximately 100 PSI as read from the cylinder regulator).

Analysis Reporting: Each laboratory should report its results within ten (10) working days of the cylinder analysis *using the report form attached*. The results should be mailed to:

California Air Resources Board
Monitoring and Laboratory Division
Michael Miguel, Manager
Quality Assurance Section
P.O. Box 2815
Sacramento, CA 95812

Quality Assurance Section staff will report the performance audit results to each participating laboratory with a summary comparing the laboratory's audit results with the NIST values.

Questions: Please direct your questions to Mr. Tim Gergen at (916) 322-7053, or via e-mail at tgergen@arb.ca.gov.

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M.3.0 POST AUDIT PROCEDURES

M.3.0.1 LABORATORY REPORTS

Upon completion of the analysis, the laboratory reports the results to the QA Section. The laboratory report (Figure M.3.0.1) includes the following:

1. Date of analysis
2. Number of runs
3. Average measured concentration
4. Standard deviation

M.3.0.2 POST AUDIT CALCULATIONS

Calculate the percent difference for each compound analyzed in the audit by comparing the reported concentrations against the NIST assigned concentrations.

$$\text{Percent Difference} = \frac{\text{Measured Conc.} - \text{Assigned Conc.}}{\text{Assigned Conc.}} \times 100$$

M.3.0.3 AUDIT REPORTS

Prepare a table showing NIST assigned concentrations, laboratory measured concentrations and the percent bias for each compound analyzed (see Figure M.3.0.2).

LABORATORY RESULTS
Biannual Performance Audit
May 2002

Laboratory: _____ Contact Person: _____
Cylinder Number: _____ Gas Chromatograph Serial Number: _____
Summary of Analytical Method Used: _____

Compound	Date of Analysis	Number of Runs	Average Conc. (ppb)	Std. Deviation
Benzene				
Bromomethane				
1,3-Butadiene				
Carbon Tetrachloride				
Chlorobenzene				
Chloroform				
1,2 Dibromoethane				
1,2 Dichlorobenzene				
1,3 Dichlorobenzene				
Dichlorodifluoromethane				
1,2-Dichloroethane				
Dichloromethane				
1,2-Dichloropropane				
Ethylbenzene				
Isoprene				
Methyl tertiary-Butyl Ether				
Styrene				
Tetrachloroethylene				
Toluene				
1,1,1 Trichloroethane				
Trichloroethylene				
Trichlorofluoromethane				
1,1,2-Trichlorotrifluoroethane				
Ortho-Xylene				
Meta/para-Xylene				
Vinyl Chloride				

Comments: _____

Within ten days of analysis, please send results to:

California Air Resources Board
Monitoring and Laboratory Division
Michael Miguel, Manager
Quality Assurance Section
P.O. Box 2815
Sacramento, CA 95812

Figure M.3.0.1
Laboratory Report

Table 1

Toxics Performance Audit Summary
California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section
2nd Quarter, 2002

Compound	NIST Cylinder # Assigned Conc. (ppb)	Bay Area Air Quality Management District				Northern Laboratory Branch -- CARB				South Coast Air Quality Management District			
		Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Diff.	Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Diff.	Meas. Conc. (ppb)	Std. Dev. (ppb)	No. Runs	% Diff.
Benzene	3.08	3.20	0.153	3	3.9%	3.21	0.080	8	4.2%	2.96	0.04	3	-3.9%
Bromomethane	1.06	n/a	---	---	---	1.08	0.06	8	1.9%	n/a	---	---	---
1,3-Butadiene	0.61	0.53	0.058	3	-13.1%	0.72	0.02	8	18.0%	0.69	0.12	3	13.1%
Carbon Tetrachloride	0.093	0.09	0.006	3	-3.2%	0.11	0.01	8	18.3%	0.07	0.03	3	-24.7%
Chlorobenzene	0.55	n/a	---	---	---	0.51	0.01	8	-7.3%	n/a	---	---	---
Chloroform	0.16	0.15	0.006	3	-6.3%	0.150	0.01	8	-6.3%	0.16	0.06	3	0.0%
1,2-Dibromoethane	0.049	0.047	0.006	3	-4.1%	0.08	0.01	8	63.3%	0.06	0.02	3	22.4%
1,2-Dichlorobenzene	0.51	n/a	---	---	---	0.53	0.03	8	3.9%	0.38	0.02	3	-25.5%
1,3-Dichlorobenzene	0.85	n/a	---	---	---	0.83	0.03	8	-2.4%	0.51	0.02	3	-40.0%
Dichlorodifluoromethane	0.99	n/a	---	---	---	n/a	---	---	---	n/a	---	---	---
1,2-Dichloroethane	0.64	0.63	0.058	3	-1.6%	0.58	0.02	8	-9.4%	0.59	0.04	3	-7.8%
Dichloromethane	8.12	8.40	0.321	3	3.4%	8.2	0.3	8	1.0%	8.61	0.24	3	6.0%
1,2-Dichloropropane	0.5	n/a	---	---	---	n/a	---	---	---	n/a	---	---	---
Ethylbenzene	2.04	1.90	0.058	3	-6.9%	1.99	0.05	8	-2.5%	1.79	0.12	3	-12.3%
Isoprene	0.84	n/a	---	---	---	n/a	---	---	---	0.78	0	3	-7.1%
Methyl tert-Butyl Ether**	8.4	8.50	0.153	3	1.2%	8.26	0.190	3	-1.7%	n/a	---	---	---
Styrene	0.32	n/a	---	---	---	0.26	0.010	8	-18.8%	0.42	0.04	3	31.3%
Tetrachloroethylene	1.03	0.97	0.029	3	-5.8%	0.92	0.03	8	-10.7%	0.98	0.03	3	-4.9%
Toluene	6.24	6.30	0.416	3	1.0%	6.14	0.06	8	-1.6%	5.68	0.02	3	-9.0%
1,1,1-Trichloroethane	3.06	3.05	0.204	3	-0.3%	3.15	0.11	8	2.9%	3.200	0.08	3	4.6%
Trichloroethylene	3.43	3.40	0.2	3	-0.9%	3.43	0.16	8	0.0%	n/a	---	---	---
Trichlorofluoromethane	1.55	1.45	0.05	3	-6.5%	n/a	---	---	---	n/a	---	---	---
Trichlorotrifluoroethane	1.15	1.12	0.046	3	-2.6%	n/a	---	---	---	n/a	---	---	---
o-Xylene	0.51	0.43	0.058	3	-15.7%	0.550	0.02	8	7.8%	0.41	0.02	3	-19.6%
m/p-Xylene*	3.66	3.80	0.153	3	3.8%	3.62	0.14	8	-1.1%	3.02	0.17	3	-17.5%
Vinyl Chloride	0.7	0.57	0.058	3	-18.6%	0.76	0.04	8	8.6%	0.65	0.11	3	-7.1%

Percent Bias = (Measured Concentration - Assigned Concentration)/Assigned Concentration X 100%
n/d = Not Detected; n/a = Not Analyzed.

* m- and p-Xylene coeluted. Reported concentration and percent bias based on the sum of m-Xylene and p-Xylene.

** Methyl tertiary-Butyl Ether laboratory measurements and assigned concentration are from NIST Certified Cylinder # ALM 063395
ARB Northern Laboratory Branch analysis values reflect concentration assignments of the laboratory working standards made by comparison to NIST reference materials received 5/98.

Figure M.3.0.2
Audit Report